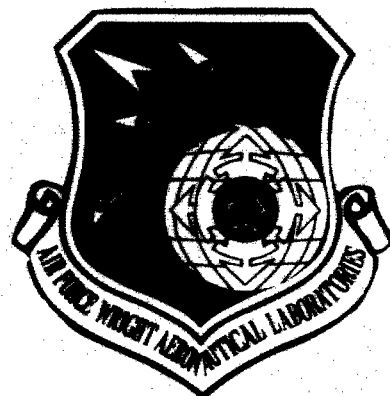# SEM STUDIES ON ABPBI/PBT CAST FILMS

A. K. Kulshreshtha and G. E. Price
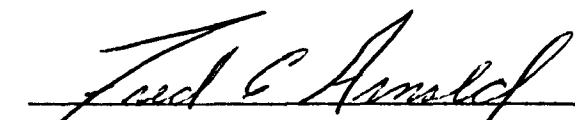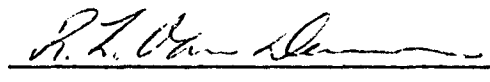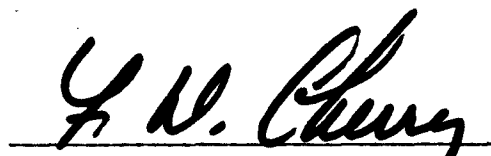University of Dayton Research Institute

April 1982

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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FRED E. ARNOLD
Contract Monitor

R.L. VAN DEUSEN, CHIEF
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER

F.D. CHERRY, Acting Chief
Nonmetallic Materials Division

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morphology	Scanning Electron Microscopy	SEM
PBT	Polyblends	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Scanning electron microscopy studies on poly-p-phenylene benzobisthiazole (PBT) a rigid rod polymer – and poly – 2,5 (6) benzimidazole, – a flexible coil polymer, – cast films indicates aggregates, or domains, rich in PBT polymer dominates the morphology. In blends containing 10-30% PBT, the shape of the aggregates or domains is ellipsoidal whereas in the 60% blend the morphology is distinctly lamellar or ribbon-like.

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FOREWORD

This report was prepared by the University of Dayton Research Institute, Nonmetallic Materials Division, Polymer Branch. The work was initiated under Air Force Contract No. F33615-81-C-5019, "Polymeric Materials for Advanced Aircraft and Aerospace Vehicles", Project No. 2419, "Research to Define the Structure Property Relationships", Task No. 24190431. It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the contract monitor. Authors were Dr. A. K. Kulshreshtha and Mr. G. E. Price, University of Dayton Research Institute, with Dr. Donald R. Wiff as the principal investigator.

This report covers research conducted from January 1980 to September 1980.

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LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

ABBREVIATIONS USED IN THIS REPORT

EV	=	Electron Volts
BSE	=	Backscattered Electron
SEI	=	Secondary Electron Imaging
KV	=	Kilo Volts
SE	=	Secondary Electron
BSEI	=	Backscattered Electron Imaging
SEM	=	Scanning Electron Microscope
CFACS	=	Charge Free Anticontamination System
MSA	=	Methane Sulfonic Acid
FNA	=	Fuming Nitric Acid
TFAA	=	Trifluoroacetic Acid
STEM	=	Scanning Transmission Electron Microscope
EDAX	=	Energy Dispersive Analysis of X-rays
PBT	=	Poly (p-phenylene benzobisthiazole)
ABPBI	=	Poly-2,5(6)benzimidazole

NOMENCLATURE

Referring to blend composition, the first percentage refers to the concentration of the coil-type matrix material (ABPBI), while the second figure represents the concentration of reinforcing rod-type polymer (PBT). Thus, a 40/60 polyblend would represent a film made by mixing 40% ABPBI and 60% PBT.

SECTION I

INTRODUCTION

The physical properties of structural polymeric materials are functions of not only the chemical structure of the polymer but also of the size, shape, packing geometry and connectivity of any heterogeneous or anisotropic regions. In the quest for new materials with specific properties, polymer blends have a great intrinsic potential. Often, a particular combination of properties is required in a structural material and this can be achieved by mixing two appropriately chosen polymers. However, it is intrinsic to polymeric systems that they are mutually incompatible and thus will defeat attempts at intimate mixing. In fact, the different polymeric constituents will segregate. The incompatibility can lead to phase separation on a microscale which can extend from angstrom level (tens or hundreds) to micron level (fraction of a micron to a few microns). Microphases occurring in blends have a significant role to play in determining the specific properties of the polymeric material. In view of the dominating influence of blend morphology in governing mechanical properties, it is necessary to set-up practical ways of studying morphology in two-phase systems and characterizing the shape, size and arrangement of the microphases and the origin of composite sturctures. The present report deals with the direct, microscopic methods of investigating blend morphology.

SECTION II

INVESTIGATIVE TECHNIQUES

BASIC OPERATION OF SEM

Whereas the electron beam in transmission microscopes is fixed, in scanning electron microscopes, it is rastered across the sample. The image is produced by collecting secondary electrons emitted from the excited surface by means of a scintillator and then reproducing the scintillator image in a CRT display syncronized with the beam sweep. Because of the larger diameter of the electron beam ($\sim$ 100 Å) resolution is less than that obtainable in transmission electron microscopes. However, extremely large depths of field are possible and relatively large samples may be examined, often with minimal preparation except for application of a conductive coating.

INFLUENCE OF CHARGE-UP ON IMAGE QUALITY

When the specimen is nonconductive material, it is negatively charged up by the electron probe, and this disturbs normal secondary electron emission. This charge-up causes some unusual phenomena such as abnormal contrast, and image deformation and shift.

Usually, the surface of a polymeric specimen (nonconductive) is coated with some conductive metal prior to observation. Rough-surfaced specimens (such as fractured polyblend films) must be evenly coated from every direction. The charge-up phenomenon which deteriorates the image quality remarkably, can be avoided by lowering the electron beam energy or coating the specimen surface with conductive metal.

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SPECIMEN DAMAGE BY ELECTRON BEAM

The loss of electron beam energy in the specimen occurs mostly in the form of heat generation at the irradiated point. Polymeric materials and biological specimens (which are generally not resistant to heat) are easily damaged by the electron probe, because of their low heat conductivity. This radiation damage can be avoided in the following manner:

    a. by using low accelerating voltage
    b. by decreasing electron beam intensity
    c. by shortening exposure time, even though it would
        reduce photograph smoothness slightly.
    d. by photographing large areas with low magnifications
    e. by controlling the thickness of coating metal on
        the specimen surface

CONTAMINATION

When the electron probe irradiates the specimen for a long time in a vacuum, the residual organic compounds in the column build up as contamination at the probe irradiation spot on the specimen surface. The contamination layer produces the following influences:

    a. the image becomes darker because of decreased secondary
        electron emission
    b. the resolution becomes lower because the contamination
        layer covers microstructures of the specimen surface
    c. the detectability of elemental analysis with x-rays
        becomes lower especially for light elements

The contamination rate can be effectively decreased by cooling the surroundings of the specimen. A liquid nitrogen trap is available for SEMs, which being cooled with liquid N_2, cools the specimen surroundings and decreases contamination rate by 90-95%.

PREPARATIVE METHOD: SPUTTER COATING

It is necessary to coat the specimen with an electrically conducting layer to prevent surface charging and to help protect it against radiation damage on exposure to the electron beam. A continuous layer of coating on the polyblend film was formed by cathodic sputtering. In the sputtering process the specimen is placed in an electrical discharge between a cathode plated with the metal to be deposited and an anode which is the specimen table. The discharge takes place in a low pressure atmosphere ($\sim 2 \times 10^{-1}$ torr) of an inert gas (argon). Variables in the process include the discharge voltage and current, coating time, gas pressure, the distance between the specimen and the cathode, and the amount of cooling applied to the specimen table. For most polyblend work involving SEM, gold-palladium coating of about 300Å thickness proved to be reasonably satisfactory.

CONTRAST INTENSIFICATION IN THE ELECTRON MICROSCOPY OF POLYBLENDS

Phase separation phenomena are commonly observed in the morphology of polymer-polymer blends. With SEM it should be possible to observe phase boundaries and analyze phase composition, particularly since currently available SEMs have a resolution of 50 Å. However, the high resolving power of the electron microscope cannot always be exploited because of inadequate contrast in the image.

Image contrast in the SEM arises mainly from the scattering of electrons at the atoms of the object. Therefore, the contrast of the electron-microscopic image is determined by the properties of the object itself, such as density, thickness

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and atomic number. If we fix the parameters of the electron microscope (aperture of the objective lens and accelerating potential) the contrast of the image increases in proportion to these properties of the object. As a general rule, the contrast increases with the atomic number Z.

Organic polymeric materials do not meet the requirement for high contrast, because their molecules consist mainly of light atoms and their density usually lies in the range 1-2g cm^{-3}. Various methods, based on treating the object with substances containing heavy atoms of high scattering power have been used to increase the contrast of electron microscopic images of organic/biological materials. Contrast materials or techniques can modify the structure as well as reveal it. Methods of contrast intensification for the electron microscopy of synthetic polymers are poorly developed and have found only limited application. Among the parameters of the electron microscope which affect the image contrast, accelerating voltage is the most important one. A decrease of image contrast with increase of accelerating potential is a general feature of electron microscopy.

ETCHING OF POLYBLEND SURFACES

The selective etching of polyblend surfaces can be a useful technique of revealing morphology. For this purpose, a liquid etchant is chosen which may selectively dissolve one of the components of the polyblend, creating surface relief and enchancing morphological contrast. Liquid etching is particularly useful in removing surface oligomers or low molecular weight fractions. Etching and microscopy often go

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hand in hand.

For the etching of ABPBI/PBT cast films, optimum etching conditions were established. This is an essential task, because at high concentrations and temperatures and long etching times, most liquids used for etching purposes are capable of dissolving, swelling or degrading the bulk of the polyblend. Under optimum conditions, however, a polyblend surface will be selectively attacked by the etchant, thus creating a desirous etching pattern. The first step in preparation for etching is determining a suitable liquid for any given polymeric constituent. The well-known Hildebrand criteria of mixing can be utilized for the proper organic solvent selection. Etching of ABPBI/PBT cast films was carried out in 70% H_2SO_4 at room temperature for period varying from 15 min. to 45 min. The etched film was neutralized with NH_4OH, washed with water and dried prior to sputter-coating for SEM examination.

BACKSCATTERED ELECTRON IMAGING

The average energy of a secondary electron is about 2 to 3 eV. When a specimen charges under the beam in the secondary electron (SE) mode, a charge accumulation of a few volts takes place. The average energy of a backscattered electron is 60-90% of the energy of the beam and can be over 20 KV for a beam energy of 25 KV. The backscattered electron (BSE) detector is much less sensitive to charge phenomena than the SE detector.

Images of higher contrast, but lower resolution can be obtained by collecting only higher energy electrons which

are backscattered from the specimen surface.

Before the arrival of the Robinson detector, backscattered electron imaging techniques were a little-used option. Beam currents were high, resolution was poor, scan speeds were slow and good results were only achieved by a few SEM specialists. Aside from spatial resolution, the problem was compounded by extremely poor signal-to-noise resulting in unacceptable micrograph quality.

The wide angle scintillator-photomultiplier type Robinson BSE detector has opened a new dimension in backscattered detection. BSE detectors feature true TV scan speeds, they have good signal-to-noise ratio amplification characteristics at low beam currents, and have consistently demonstrated a resolution capability of better than 100 Å. Because of the large solid angle obtained with the detector at the specimen surface, a very efficient collection of backscattered electrons is accomplished. The signal to noise ratio is actually higher than with the secondary electron detector. This results in extremely high back-scatter resolution, similar to that obtained in the secondary mode. This is possible because now beam currents of 1×10^{-12} amps and spot sizes of 60 Å can be utilized for sufficient backscattered collection. Also, since the Robinson BSE detector is placed directly above the specimen, shadowing effects which are normally present with BSE detectors are eliminated. It is a well known fact that BSE co-efficient is proportional to atomic number. The higher the atomic number, the higher the yield of backscattered

electrons. With the Robinson BSE detector, one can observe concentration differences within the same atomic number of about 0.5%. For the first time this allows for the observation of compounds. Used in conjunction with an energy dispersive x-ray analyzer, there lies a powerful tool for increasing the speed and the accuracy of analytical capabilities.

The advantages of BSE detectors over SE detectors are summarized below:

    a.   Elimination of charging artifacts
    b.   Reduced edge highlighting
    c.   Easier imaging of difficult specimens
    d.   Best atomic number contrast
    e.   TV scan speeds

SECTION III

APPLICATION AND RESULTS

The two-phase morphology in ABPBI/PBT cast films becomes apparent when the films are freeze-fractured using liquid nitrogen and subsequently examined with a scanning electron microscope. The fracture electron micrographs shown in Figure 1 illustrates this clearly, where the influence of blend composition on morphology can be examined. In blends of various composition, the effect of phase separation can be seen. The cross-section of 90/10 blend shows a honeycomb-like matrix (presumably ABPBI) which surrounds the domains or "aggregates" of rod-like PBT molecules. In the 80/20 blend, the matrix now looks somewhat different and "spongy" in appearance. The embedded aggregates look more round (elliptical rather than disk-shaped). When the rod content in the blend is increased to 30% (i.e. in the 70/30 blend), a shape of aggregates again becomes platelet or disk-type and the matrix has a rough, compact texture, very different from the smooth texture seen in 90/10 blend. In all these blend films, the adhesion between the aggregates and the surrounding matrix appears to be poor and the interphase boundaries look sharp. When the blend composition is changed to 40/60, one can no longer easily distinquish between the aggregates and the matrix material. It appears that the morphology has undergone a transition from droplet-type (e.e. spherical) to ribbon-type (i.e. lamellar) as the blend composition is changed from 90/10 to 40/60. Also, the contrast between the

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Figure 1.   Fracture Morphology of Polyblends Cast
            from MSA.

dispersed phase (i.e. the aggregate) and the continuous phase (i.e. the matrix) seems to vanish in the micrograph of the 40/60 blend. Surface topologies of these films are compared in Figure 2. The texture of the film surface is different for each blend composition; however, no aggregates are visible on the surface.

The micrographs shown in Figure 3 show an interesting comparison of the spherulitic boundaries observed in ABPBI and in 90/10 and 70/30 blends. Such features have not been observed in the 40/60 blend, suggesting a fundamental transition in morphology (e.g. from a spherical to a dispersed crystallite morphology) as a result of increasing concentration of PBT in the blend.

Even though the regions or the domains containing the disperse phase (PBT) are not visible on the surface of 90/10 and 80/20 polyblend films, they might be buried beneath the surface. Solvent-etching appears to be a promising way to reveal these domains, provided a solvent can be found in which the two polymers have different solubility (selective solvation). Figure 4 shows the effect of etching the surface of 90/10 blend with 70% aqueous sulfuric acid, for two different etching times. It is seen that even after 15 min. of etching, the original spherulitic texture of film surface has disappeared and some humps are seen outlining the presence of aggregates. When the etching time is increased to 30 min., the surface of the etched film shows a large number of aggregates, oriented at random, and having a distribution of sizes varying from 0.5μ to 3μ.

90:10

80:20

70:30

40:60

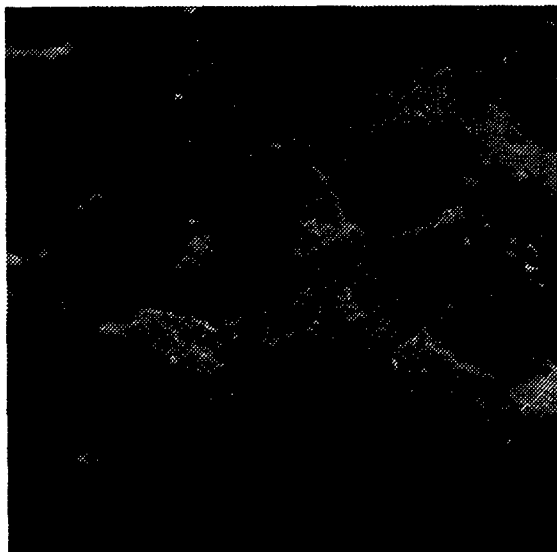Figure 2.   Surface Morphology of Polyblends Cast
from MSA.

ABPBI Film

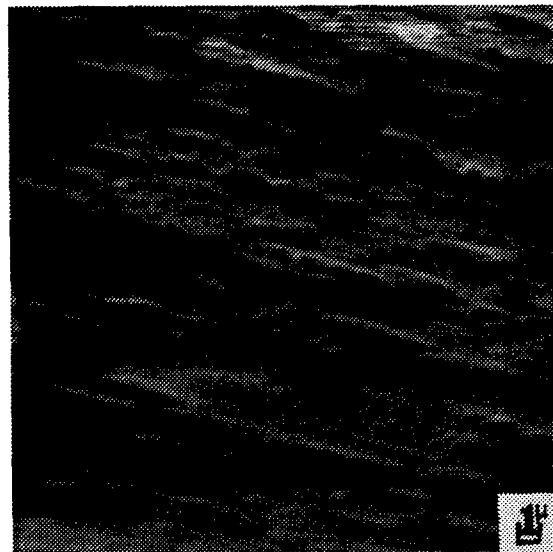90:10 Polyblend Film   70:30 Polyblend Film
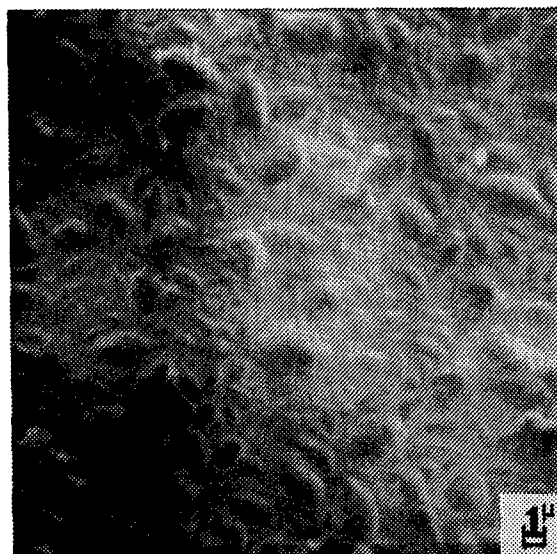
Figure 3.   Spherulitic Surface Morphology Films
             Cast from MSA.
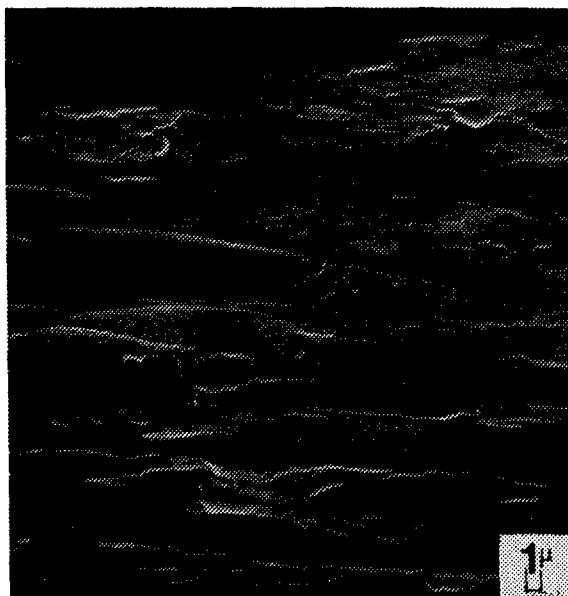
13

Etching time: 0 min.

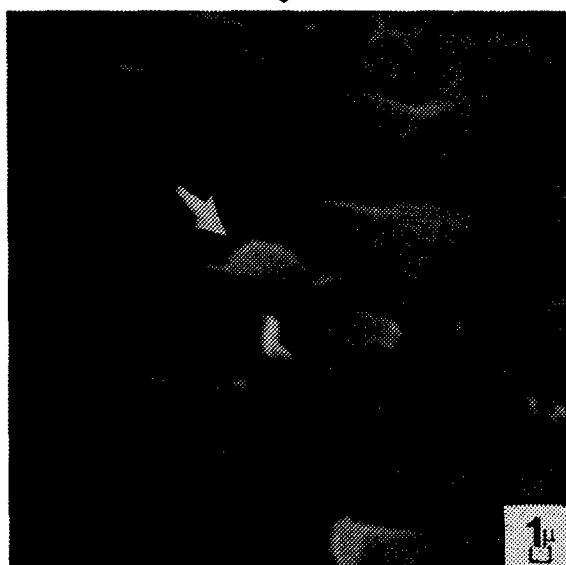Etching time: 15 min.

Etching time: 30 min.

Figure 4. The Influence of Acid-Etching Material: ABPBI-PBT Blend: 90/10, Cast with MSA Etching Agent: 70% H_2SO_4.

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Since PBT macromolecules contain sulfur and ABPBI does not, it is possible to carry out an elemental analysis (using the emitted x-rays in the SEM) on the etched films showing domains on the surface. Such an enquiry would reveal information on the composition of the domains. Energy-dispersive x-ray analysis (EDAX) was carried out on a 80/20 blend, etched for 30 min. and subsequently neutralized. The dot maps of sulfur did not show a relief corresponding to domain boundaries. However, an x-ray mapping of sulfur at a domain and beside it (Figure 5) give different peak ratios (sulfur/coating). Qualitatively, the evidence points that there is a greater concentration of sulfur inside the domains than in the area surrounding them. This analysis, though useful for inference, has its limitations. Any approach to define the internal morphology of domains would involve a study of microtomed sections of the blend film by EDAX and microdiffraction using a Scanning Transmission Electron Microscope (STEM).

Figures 6 and 7 summarize the morphologies observed in 90/10 and 40/60 blend films respectively. There are surface cracks visible on the surface of the 40/60 blend film (Figure 7a). A higher magnification picture of these cracks high-lights the layered structure of the 40/60 polyblend film (Figure 7b). Even higher magnification (30000X) reveals that individual layers consist of parallel ribbon-like microfibrils of 150 Å width (Figure 8). The ribbons within a given layer are parallel to each other, but their directions
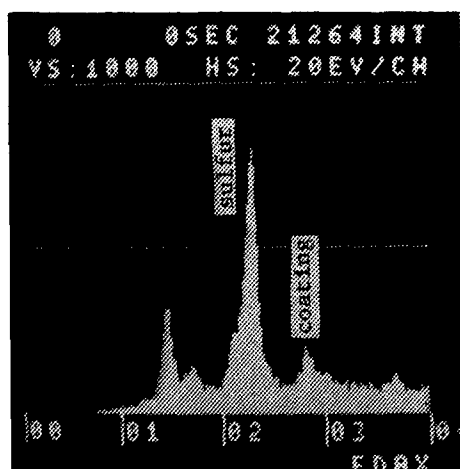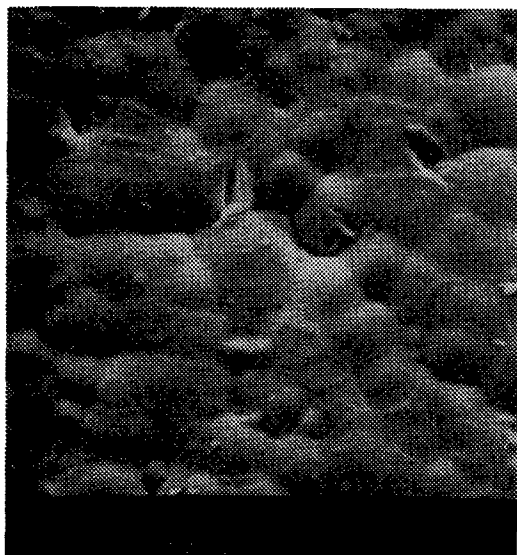
80:20 blend (MSA-CAST film)

Mapped next to an aggregate

Etched with70% H_2SO_4 for 30 min
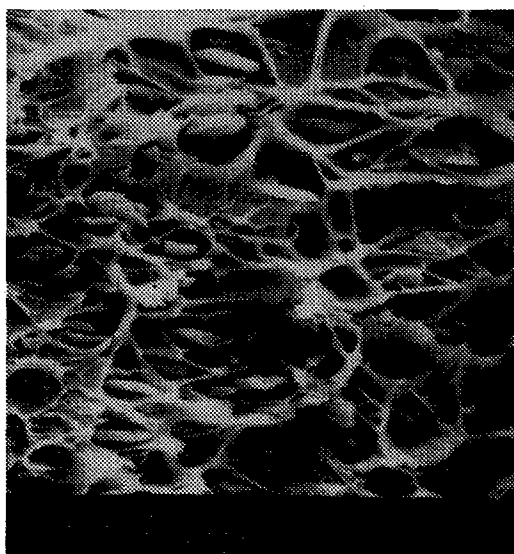
Mapped on an aggregate

Figure 5.   Surface Analysis.

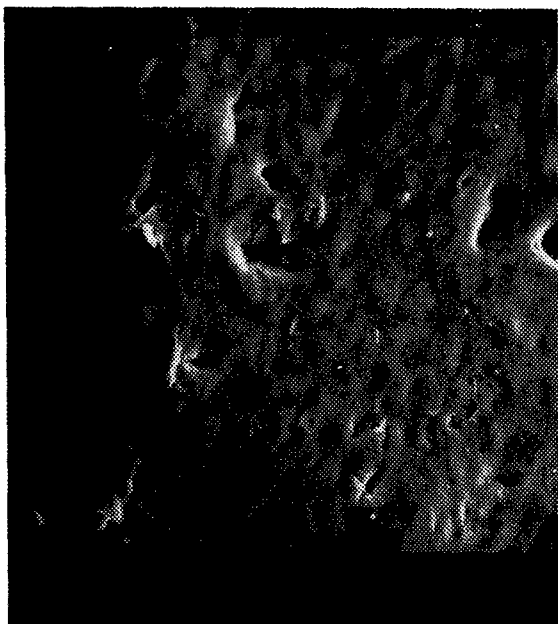**Surface**

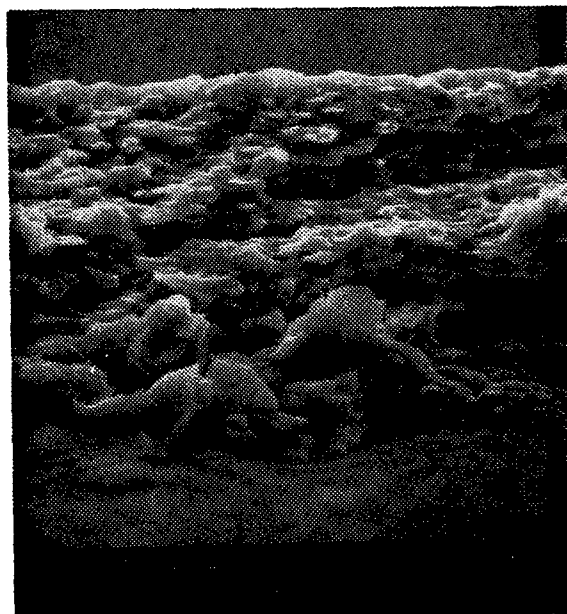**Edge**

Figure 6.   Morphology of 90:10 Blend of ABPBI-PBT
            Cast from MSA.
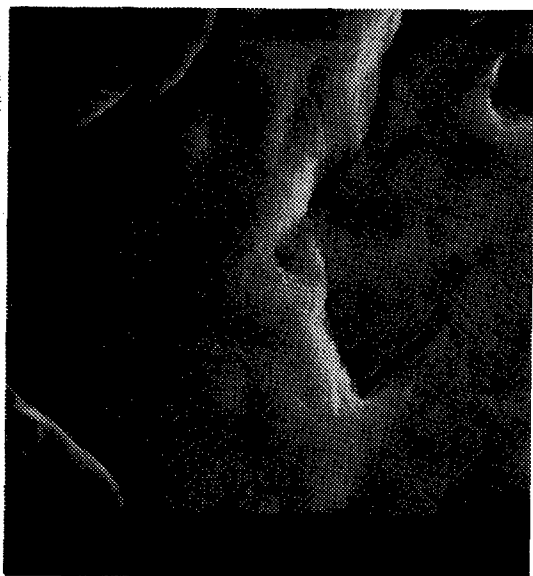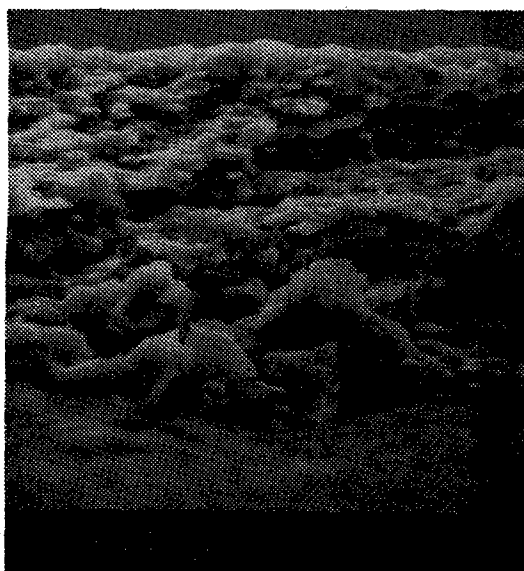
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Surface

Edge

Figure 7(a).   Morphology of 40/60 Blend Cast
from MSA.

Surface

Edge

Figure 7(b).   Morphology of 40:60 Blend of ABPBI-PBT
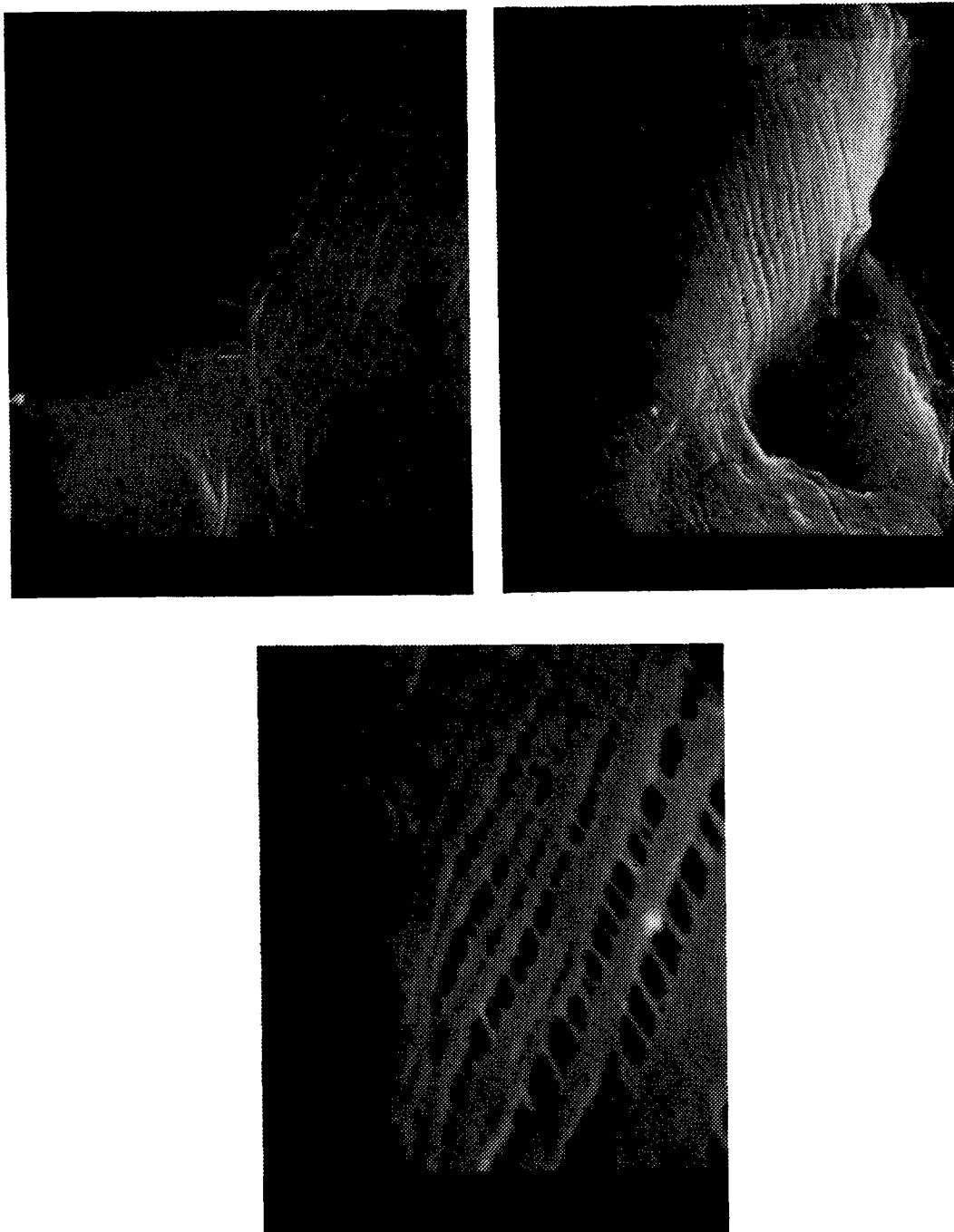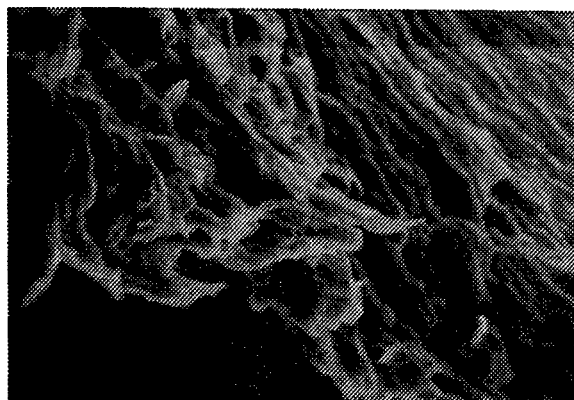   Cast from MSA.

Figure 8. Surface Morphology of 40:60 Blend
Cast from MSA.

in successive layers are different. The layers are stacked up in such a way that their overall orientation of ribbons is random. This morphology is highly reminiscent of the morphology observed in cholesteric liquid crystals.
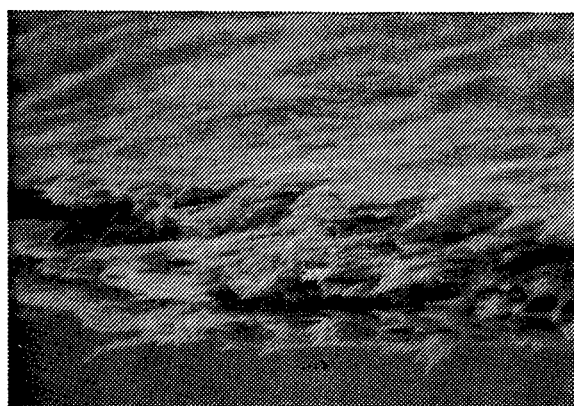
Figure 9 shows a glimpse of the morphology in the 40/60 polyblend, viewed from the edge direction. This lamellar structure is preserved even after a high temperature annealing of the polyblend film under vacuum. (Fig. 9).

Neutralizing of the as-cast polyblend film with ammonium hydroxide causes a visible shrinkage in film dimensions. This shrinkage is manifested as "wrinkles" in the surface micrographs of 80/20 and 40/60 polyblends. (Figure 10).
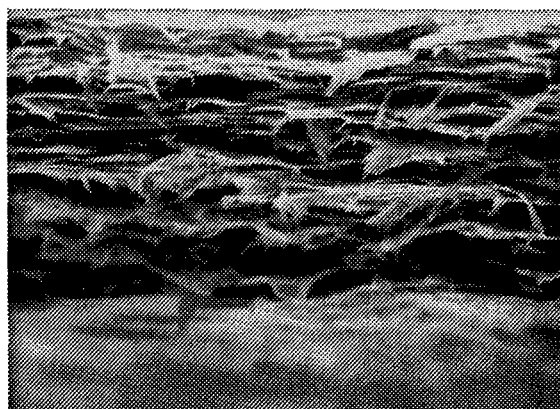
As discussed in the techniques section of this report, the technique of backscattered electron imaging (BSEI) appears to have a potential in highlighting atomic number differences between phases. A comparison of backscattered electron images (BSEI) with the conventional secondary electron images (SEI) on the same areas of films has therefore been carried out. The blend films were neutralized and coated with carbon, in order to prevent the influence of metal coating on image contrast and yet prevent a charging of specimen. Figure 11 shows a comparison of SEI and BSEI images on the 80/20 polyblend film. It is very impressing to see a contrast between the continuous and disperse phases in the backscattered image. (The brighter areas obviously represent regions rich in sulfur). It is possible to infer the shape and size of the dispersed phase (aggregates) from the BSEI micrograph. A
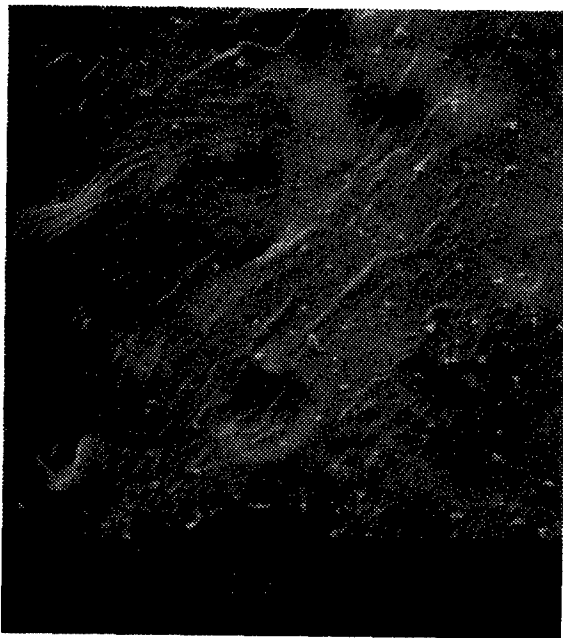
21

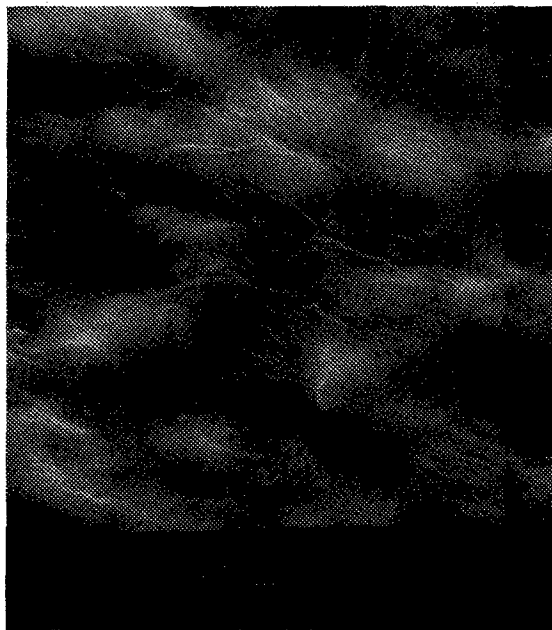As-Cast Film,
Mag. 300x

As-Cast Film,
Mag. 1000x

Film annealed at 500^{0}C
Mag. 2000x

Figure 9.   Lamellar Morphology in Blends Casting
            Solvent: MSA, Specimen: 40/60 Polyblend.
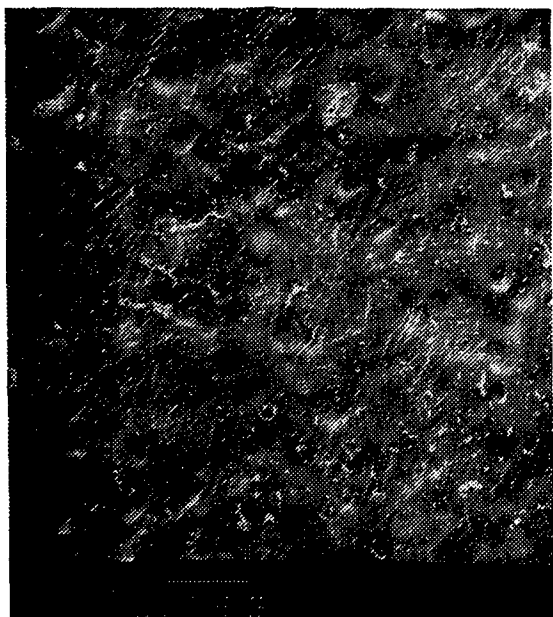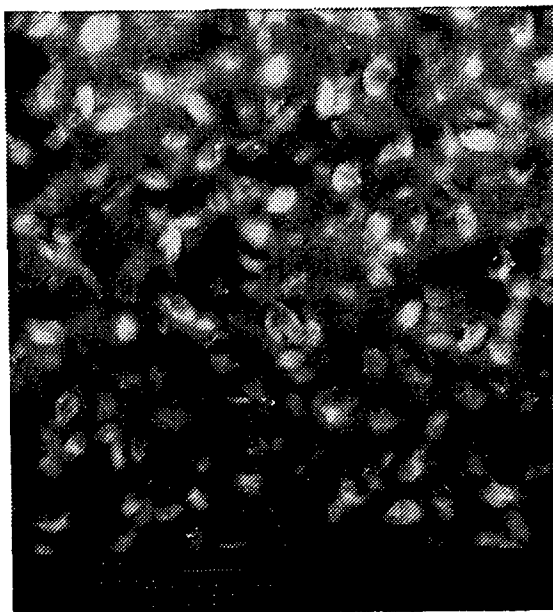
80:20 Polyblend

40:60 Polyblend

Figure 10. Surface of Neutralized Cast Films Shows
the Presence of Wrinkles! Specimens:
Film Cast from MSA.

Secondary electron imaging
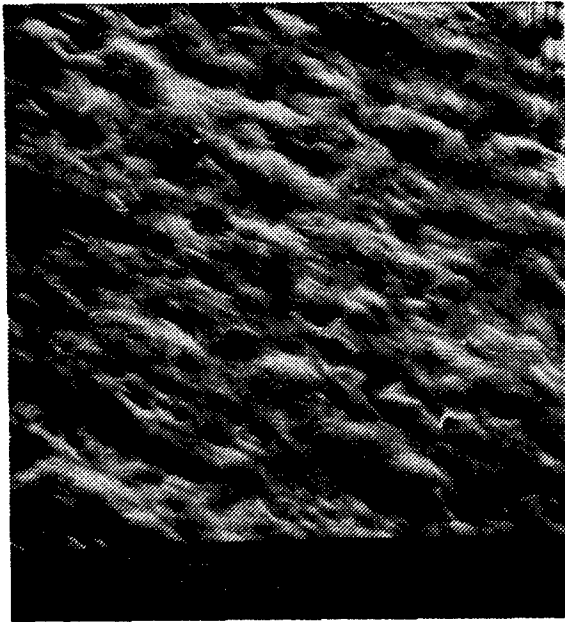

Backscattered electron imaging

Figure 11. A Comparison of Micrographs Obtained by
           Two Different Imaging Methods, Specimen:
           80/20 Blend of ABPBI & PBT Cast with
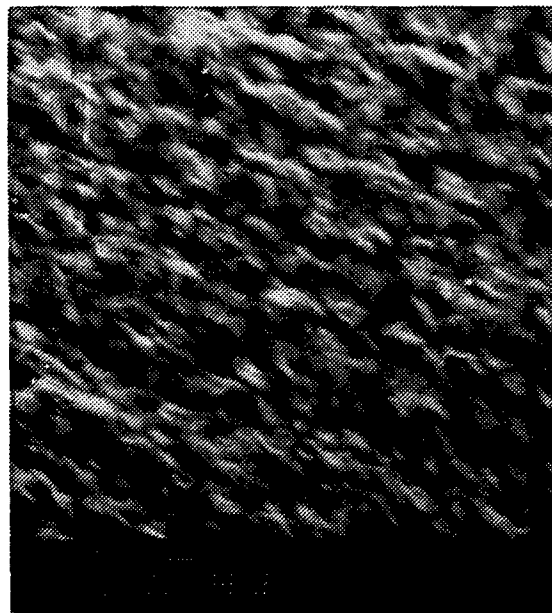   MSA, Neutralized.

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comparison of SEI and BSEI images of the same area (Figure 11) indicates that the backscattered detection leads to a tremendous gain in image contrast at the expense of resolution. This technique of BSEI has thus considerable advantage in studying the morphology of polyblends where there is a natural deficiency in contrast (see Introduction). It is a useful technique of mapping areas of different elemental (e.g. sulfur) concentration. The technique of BSEI has an advantage over the etching technique in that it is quicker and requires minimum sample preparation and handling.

A comparison of SEI and BSEI images for the 40/60 blend film is shown in Figure 12. Again, the BSEI image shows enhanced contrast, but the morphology is not so dramatic as in the 80/20 blend. This is to be expected since the concentrations of the two polymers are nearly equal and it is difficult to say which polymer forms the continuous phase and which one forms the disperse phase. Furthermore, as previously observed, a spherical-to-lamellar morphological transition has occurred within this blend, which complicates the observed morphology.

The effect of different casting solvents on the morphology has been investigated by studying the micrographs of ABPBI/PBT polyblends cast from fuming nitric acid (FNA) and comparing them with micrographs obtained earlier on MSA-cast films. Figure 13 shows the surface and fracture micrographs of the 80/20 blend film cast from FNA. The surface texture of this film is rough and granular. The fracture surface shows a honeycomb structure
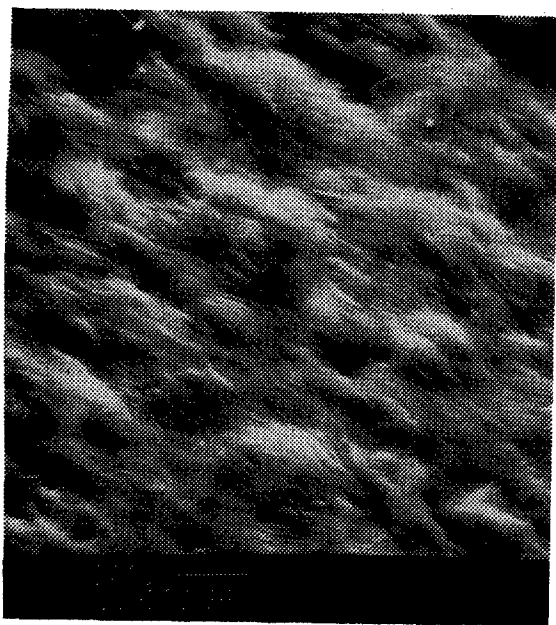
25

Secondary electron imaging

Backscattered electron imaging

Figure 12(a). A Comparison of Micrographs Obtained
by Two Different Imaging Methods
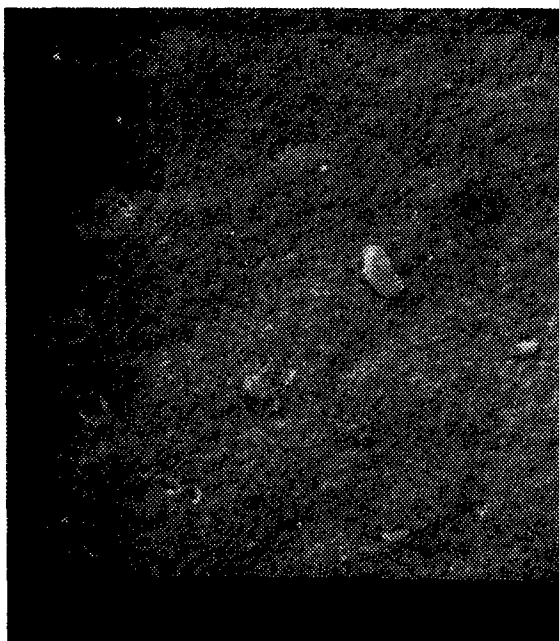Specimen: 40/60 Blend, MSA-Cast
Neutralized.

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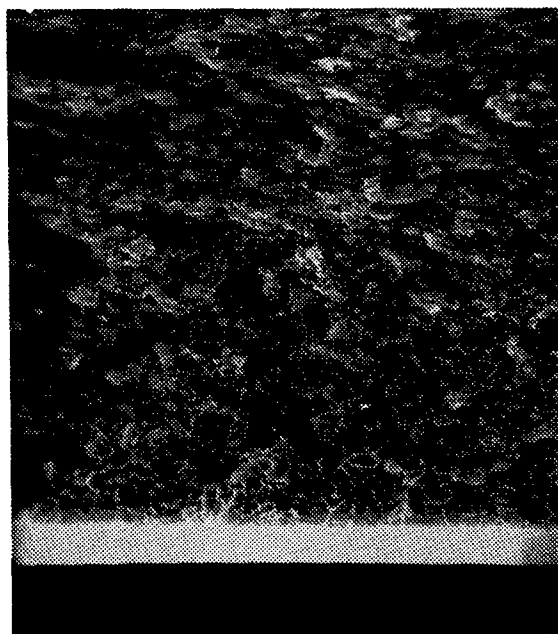**Secondary electron imaging**

Backscattered electron imaging

Figure 12(b). A Comparison of Micrographs Obtained by
Two Different Imaging Methods, Specimen:
40/60 Blend of ABPBI & PBT Cast with
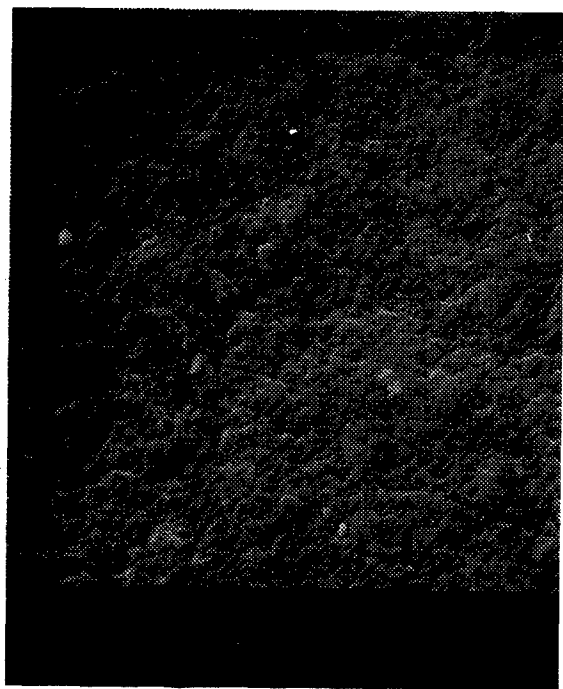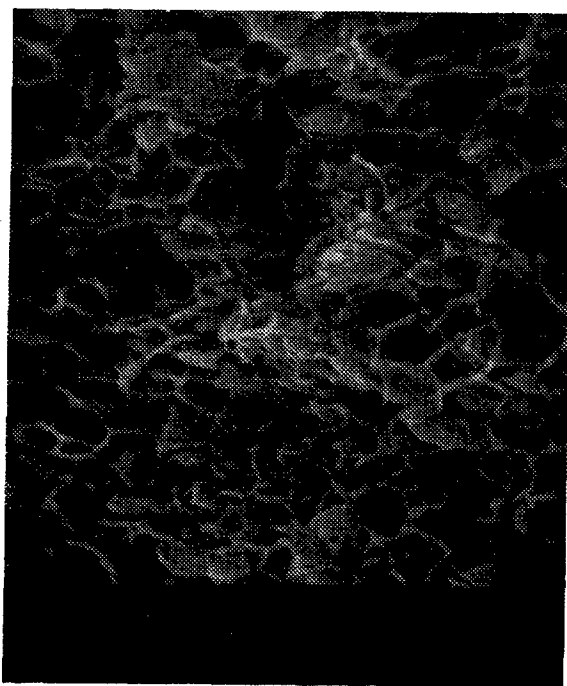MSA, Neutralized.

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Surface

Edge

Figure 13(a). Morphology of 80:20 Blend of ABPBI-PBT
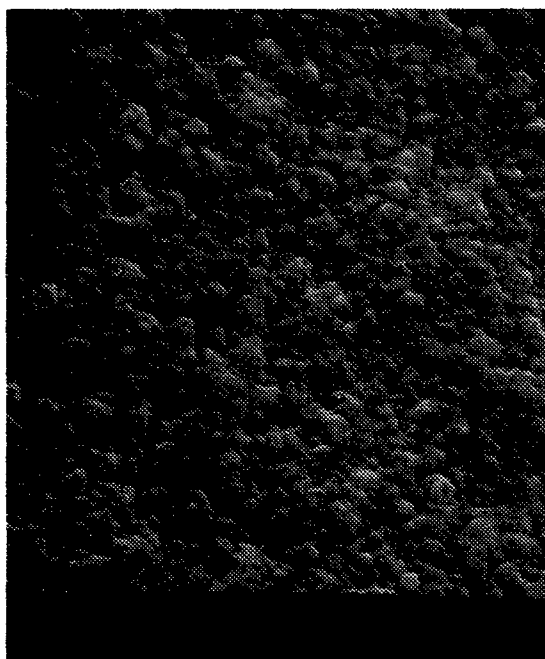Cast from Fuming HNO_3.

Surface

Edge

Figure 13(b). Morphology of 80:20 Blend of ABPBI-PBT Cast from Fuming HNO_3.
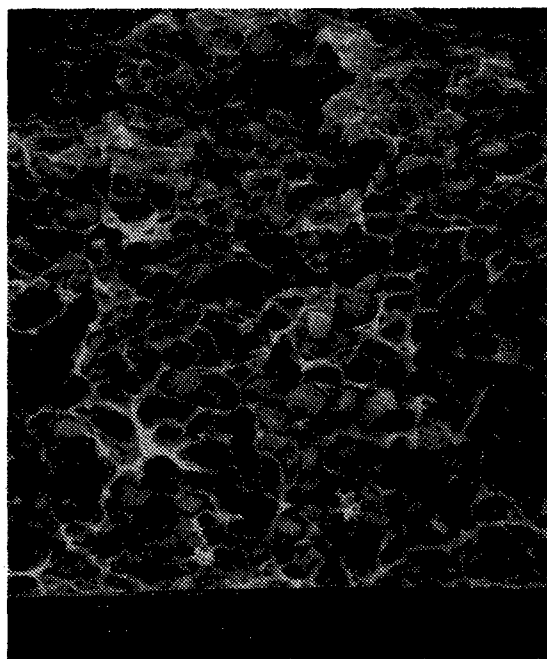
observed previously in MSA-cast films (e.g., in Figure 6). It
is possible to see entities embedded in this honeycomb-
like matrix (Fig. 13a). The fracture micrograph of the same film
obtained after neutralizing (Fig. 14) clearly shows entities
which are sitting in different shells. Thus, essentially the same
morphology is observed in FNA-cast 80/20 polyblend as was
observed earlier in the corresponding MSA-cast film.

Figure 15 shows the surface and cross-section of the 40/60
blend film which has been cast from FNA. The surface of this
film is highly uniform and does not show granular characteristics
seen in the 80/20 blend. The fracture surface of this specimen
reveals a lamellar morphology (Fig. 15), which is similar to
the morphology found in the MSA-cast film.

Various drastic aftertreatments were carried out on the
80/20 as-cast film, in order to explore the possibility of
eliminating the aggregates and obtaining a different morphology
altogether. Freeze-drying, in particular, is known to lead to
a homogeneous morphology in polyblends. For instance, the
blends of poly(methyl methacrylate) and poly (vinyl acetate)
are heterogeneous when cast in solvent, but become fairly
homogeneous when freeze-dried. The 80/20 cast film (which
contains about 30% MSA) was solvent-exchanged over several weeks
to: methanol, 50/50 methanol/benzene, benzene, and
subsequently freeze-dried. The fracture surface of the freeze-
dried ABPBI/PBT film still shows aggregates (Figure 16), although
they appear to be flaky in appearance. Another aftertreatment
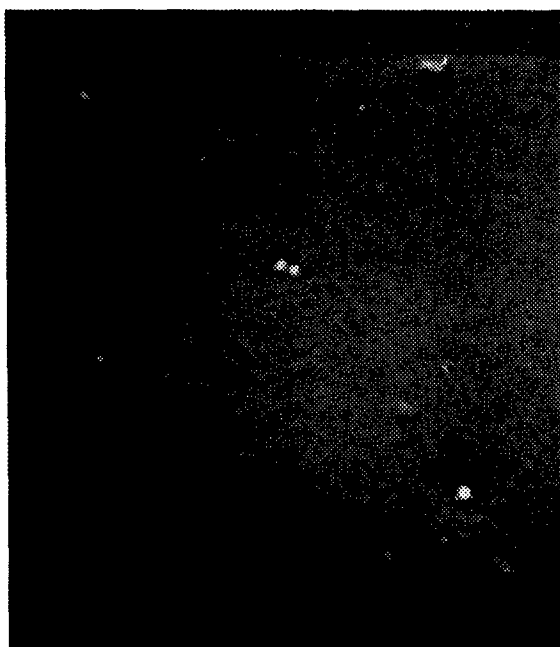given to the as-cast film is annealing under vacuum, which results

Surface

Edge
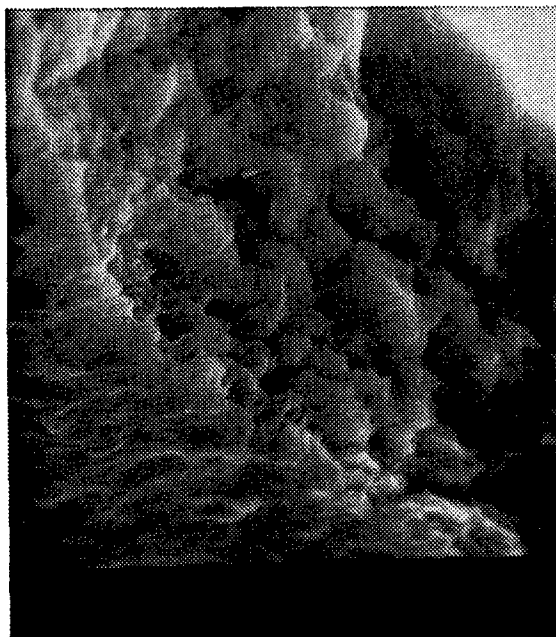
Figure 14.   Morphology of 80:20 Blend of ABPBI-PBT
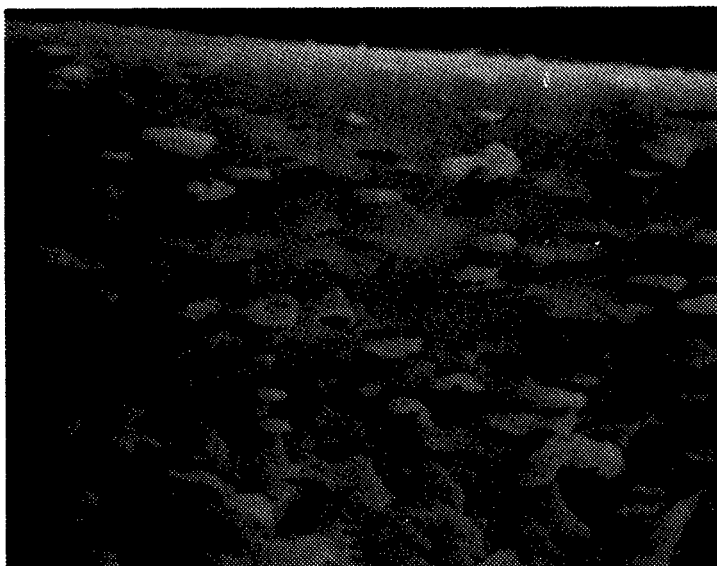 HNO_3-Cast, Neutralized.

Surface

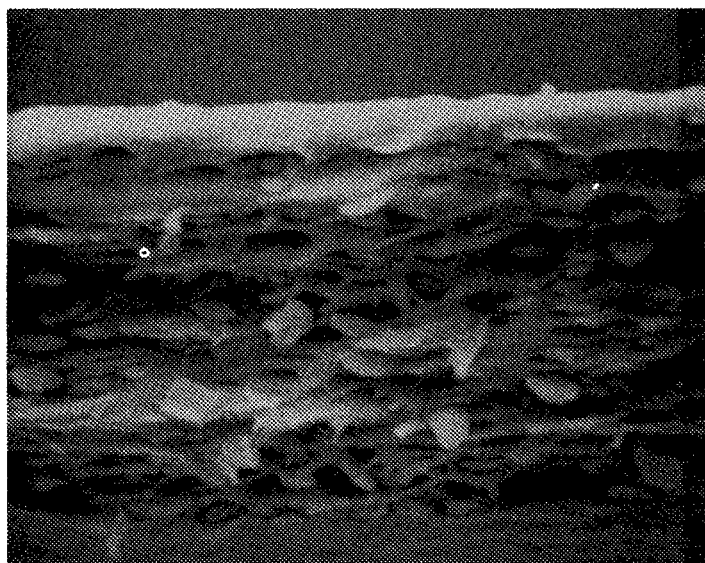**Edge**

Figure 15.   Morphology of 40:60 Blend of ABPBI-PBT
Cast from Fuming HNO$_3$.

Annealed at 500°C for 5 min.

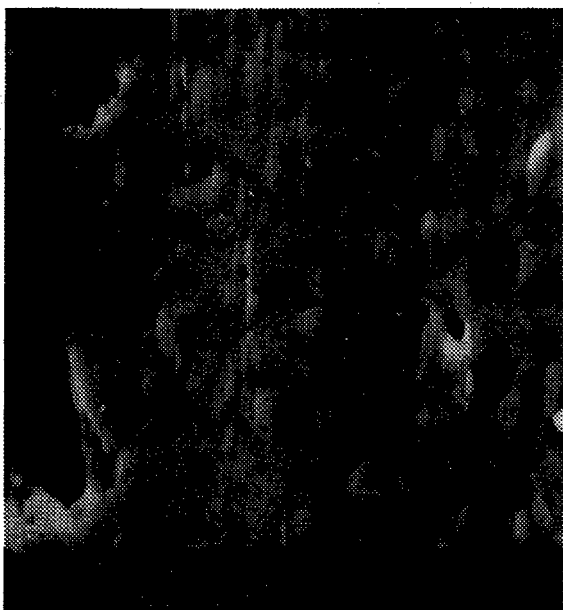Solvent - exchanged with CH_3OH/C_6H_6 and freeze-dried

Figure 16. Effect of Various Aftertreatments on Morphology Specimen: 80/20 Polyblend Film, Cast from MSA.

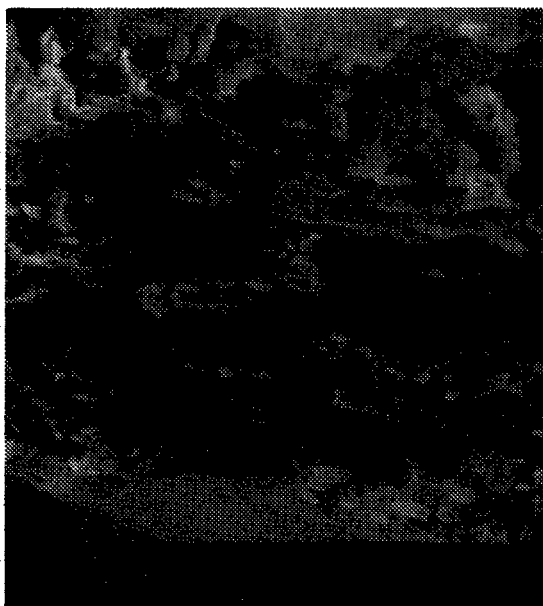in an increase in crystallinity and modulus of the film.

Figure 16 shows the edge view of the morphology of annealed 80/20 film; the aggregates are still present. In fact, the contrast between the entities or aggregates and the surrounding matrix in the polyblend has improved due to annealing. This can be attributed to a crystallization of the rod-like molecules and an randomization of the ABPBI molecules in the matrix upon annealing.

During the attempts which were made to improve the crystallite orientation in polyblends by solvent-stretching, a new solvent for ABPBI was discovered. This solvent is trifluoroacetic acid (TFAA) and caused ABPBI to soften and gel immediately after contact. With the help of TFAA, cast polyblend films of various blend composition were stretched to 100-200% stretch levels over initial length. It was expected that there may be a drastic change in morphology of cast films subsequent to this aftertreatment. However, the morphology of TFAA-stretched film still shows aggregates (Figure 17), on the surface as well as in the cross-section of the film. The appearance of aggregates on the surface of the TFAA-stretched film is attributed to an "etching" of the film surface by TFAA.

Finally, Figure 18 shows a collection of various fracture micrographs obtained from different polyblend films. The purpose of this figure is to illustrate with micrographs that different morphologies (e.g., single-phase, two-phase, lamellar or spherical) can be obtained by varying the blend composition or the processing technique.
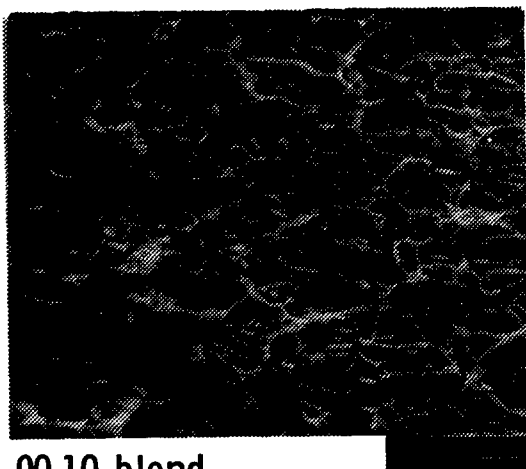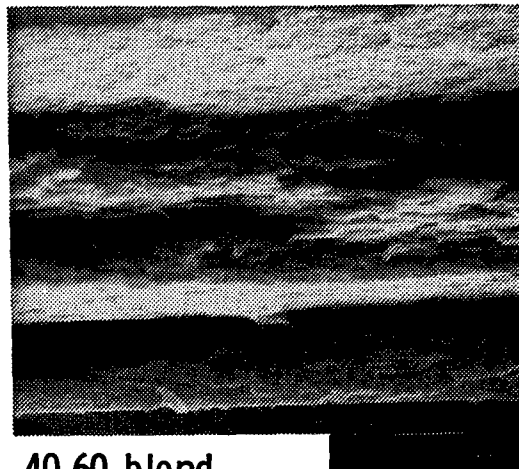
Surface

Edge

Figure 17. Effect of Aftertreatment on Morphology
Specimen: 80/20 Polyblend Cast from MSA,
Stretched 150% with Trifluoroacetic Acid.

90:10 blend
(MSA-cast)

40:60 blend
(HNO$_3$-cast)

40:60 blend,
MSA-cast, neutralized

80:20 blend,
shear-quenched,
neutralized

Figure 18. Fracture Micrographs (Miscellaneous).

SECTION IV
CONCLUSIONS

1. The cast polyblends have a two-phase morphology, i.e. they exhibit a continuous phase and a dispersed phase.

2. In blends containing 10-30% PBT, the morphology is spherical, i.e., resembling an oil-in-water emulsion. The shape of the aggregates (synonymous with "domains" or the "dispersed phase") is elliptical. The surface micrographs of these blends show a spherulitic structure, characteristic of ABPBI cast film.

3. Etching the surface of cast polyblend films with 70% H_2SO_4 or CF_3COOH (TFAA) reveals the aggregates.

4. A preliminary surface analysis using the EDAX technique shows that these aggregates are rich in sulfur. In other words, PBT molecules dominate the aggregates while the matrix appears to be formed by the flexible ABPBI molecules.

5. In the 40/60 polyblend the morphology is distinctly lamellar or layer-like. Individual lamellae consist of parallel bundles or ribbons, each of which is 150Å wide. However, the direction of orientation of the ribbons varies from one lamella to another so that the overall ribbon orientation in the film is random.

6. The neutralized cast films exhibit wrinkles on the surface, which are a manifestation of shrinkage of the film during the neutralizing process.

7. The technique of backscattered electron imaging (BSEI) leads to enhanced image contrast in surface micrographs. Using BSEI, it has been possible to see the two-phase morphology and the aggregates in cast films with minimal sample preparation.

8. Two-phase morphology is observed even when the polyblend films are cast in a different casting solvent. For example, the 80/20 blend cast with fuming HNO_3 shows aggregates of elliptical shape, dispersed in a honeycomb-shaped matrix of ABPBI. The 40/60 polyblend cast with fuming HNO_3 displays a lamellar morphology.

9. Various aftertreatments to the MSA-cast polyblend films, such as freeze-drying, annealing, or solvent-stretching with TFAA, do not eliminate the two-phase morphology and still show aggregates dispersed in a matrix.

10. Morphology can be tailored or "engineered" by varying the blend composition, the casting solvent and the method of processing the film. Molecular weight may be another important variable in governing the morphology and its effect on morphology of ABPBI/PBT, polyblends would be the subject of a future technical report.

SECTION V
FUTURE RESEARCH

While the presence of aggregates (rich in the content of PBT) as a dispersed phase in a matrix (presumably of ABPBI) has been inferred by the present work, there are still many questions which need to be answered. Some of these are:

1. What is the exact composition of the material inside the aggregates and in the area surrounding them? Are the aggregates composed entirely of rod-like molecules (PBT)? If so, is the arrangement of rod-like molecules within the aggregate well ordered?

2. Is the MSA solvent preferentially bound within the aggregates? Does the diffraction from an area within the aggregate come from the formation of a polymer-solvent complex?

3. What is the morphology of the material within the aggregate? How can rod-like molecules pack parallel to one another and still form a football-shaped aggregate? Are these aggregates, or domains, nematic? If so, how does one account for the random orientation seen in the x-ray diagrams of as-cast films?

4. Is the matrix amorphous and rich in ABPBI?

Most of the above questions can be answered by performing a microanalysis on the microtomed ultrathin slices of cast films using a STEM (Scanning Transmission Electron Microscope). Microdiffraction and imaging on precise locations within the polyblend specimen will be of great assistance in answering these questions. Furthermore, EDAX (i.e., energy dispersive x-ray analysis) can be more quantitative and meaningful when carried out with STEM.

Another experimental sophistication which would be a great practical value in improving the scope of SEM analysis on polyblend films would be the addition of a Robinson Backscatter Detector and a Charge Free Anticontamination System to the present SEM equipment currently available.